

# **Particulate Organic Matter-Contaminant Associations at the Water-Sediment Interface: Biological and Physical Controls**

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Award #N00014-96-1-0062

## **LONG-TERM GOAL**

The overall goal of this study is to build a framework for understanding processes influencing the association of contaminants with naturally occurring organic materials associated with suspended particles and surficial sediments. Specifically, we are using geochemical tracers, so-called "biomarkers", coupled with distributions of polycyclic aromatic hydrocarbons (PAHs) to identify sources of organic matter in the southern Chesapeake Bay (CB) and to understand the delivery, transformation and accumulation of natural and contaminant organic matter in coastal sediments.

## **SCIENTIFIC OBJECTIVES**

The objectives of this project are: (1) to evaluate spatial and temporal variations in organic matter delivery and degradation processes in coastal waters, (2) to relate the composition of organic matter in sediments to physical and biologically-mediated transport processes in estuarine and coastal systems, and (3) to examine links between the fluxes and cycling of natural organic matter at the water-sediment interface and the transport and fate of organic contaminants. Within this framework, we will quantify various organic contaminants associated with sedimentary particulate matter, determine the seasonal fluxes of these substances at the water-sediment interface, and establish relationships, as possible, between natural organic matter and organic contaminant cycling in coastal and estuarine systems.

## **APPROACH**

Our goal is to investigate factors (organic matter and sediment composition) influencing the distribution of a class of organic contaminants relevant to Navy interests, the polycyclic aromatic hydrocarbons (PAHs). To accomplish this, spatial and temporal variations in the concentrations of PAHs associated with suspended particles and surficial sediments were quantified at five sites in the southern Chesapeake Bay. Complementary to the PAH analyses we determined the composition of particulate organic matter using elemental and molecular analyses. Specifically, total organic carbon (TOC, C/N ratios,  $\delta^{13}\text{C}_{\text{oc}}$ ),  $\delta^{15}\text{N}$ , photosynthetically-derived carbon (inferred from chlorophyll *a*), total lipid, and two classes of lipid biomarker compounds (fatty acids and sterols) were used to determine the sources and reactivity of the particulate organic matter.

<b>Report Documentation Page</b>			<i>Form Approved OMB No. 0704-0188</i>					
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1. REPORT DATE <b>1998</b>	2. REPORT TYPE	3. DATES COVERED <b>00-00-1998 to 00-00-1998</b>						
<b>4. TITLE AND SUBTITLE</b> <b>Particulate Organic Matter-Contaminant Associations at the Water-Sediment Interface: Biological and Physical Controls</b>			5a. CONTRACT NUMBER					
			5b. GRANT NUMBER					
			5c. PROGRAM ELEMENT NUMBER					
<b>6. AUTHOR(S)</b>			5d. PROJECT NUMBER					
			5e. TASK NUMBER					
			5f. WORK UNIT NUMBER					
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> <b>Virginia Institute of Marine Sciences, School of Marine Science, Gloucester Point, VA, 23062</b>			8. PERFORMING ORGANIZATION REPORT NUMBER					
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>			10. SPONSOR/MONITOR'S ACRONYM(S)					
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)					
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> <b>Approved for public release; distribution unlimited</b>								
<b>13. SUPPLEMENTARY NOTES</b> <b>See also ADM002252.</b>								
<b>14. ABSTRACT</b>								
<b>15. SUBJECT TERMS</b>								
<b>16. SECURITY CLASSIFICATION OF:</b> <table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 33.33%; padding: 2px;">a. REPORT <b>unclassified</b></td> <td style="width: 33.33%; padding: 2px;">b. ABSTRACT <b>unclassified</b></td> <td style="width: 33.33%; padding: 2px;">c. THIS PAGE <b>unclassified</b></td> </tr> </table>			a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>	<b>17. LIMITATION OF ABSTRACT</b> <b>Same as Report (SAR)</b>	<b>18. NUMBER OF PAGES</b> <b>5</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>						

## WORK COMPLETED

During FY1998 we completed PAH analysis on all suspended particle and surficial sediment samples collected during our 1996-1997 field study. In addition, we completed our examination of the organic composition of these samples using biomarkers (stable carbon and nitrogen isotopes and two classes of lipids-- fatty acids and sterols). Our sample set included seasonal collections of two sample types obtained from each of five locations in southern Chesapeake Bay (CB): (1) suspended particles collected from two depths (1m below the surface and 1m above bottom) and (2) surficial sediments. This work focused on sites within the CB Mainstem, at the mouths of two tributaries draining into the lower CB (York and Rappahannock Rivers), and a riverine site (Claybank in the York R.; hereafter YR POD). In addition, surficial sediments were further characterized by measurements of mineral surface area and refractory (soot) carbon (carbon released following heating to 350°C; modified from Gustafsson et al., 1997).

## RESULTS

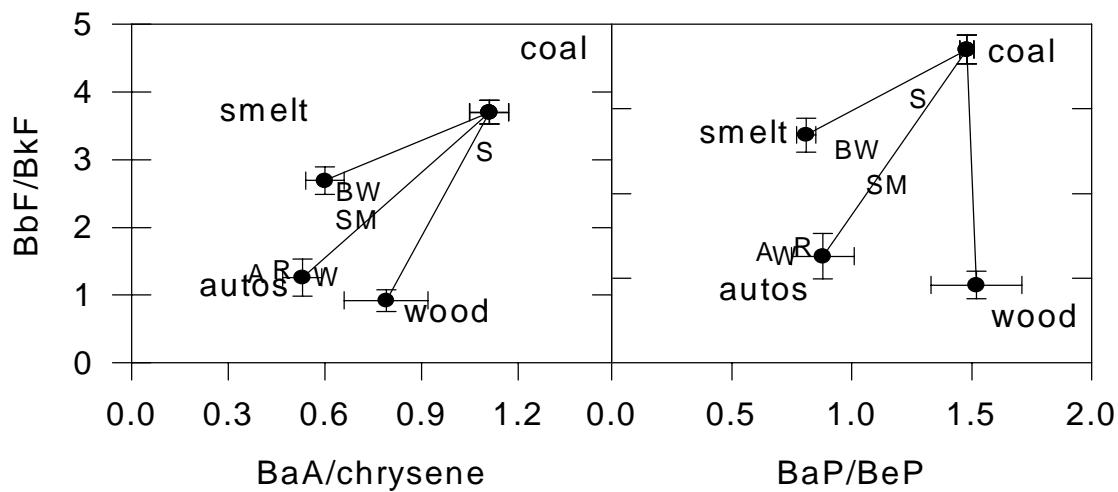
### PAH Distributions and Sources to the Chesapeake Bay

One of the most striking aspects of our PAH data set is its homogeneity. With few exceptions, concentrations of PAHs showed little spatial and temporal variation. Fluctuations in concentrations (ng L<sup>-1</sup>) are largely explained as resulting from fluctuating particle concentrations. As a result, when PAH concentrations were normalized to total suspended particle (TSS) concentrations and/or particulate organic carbon concentrations (POC), PAH concentrations were relatively constant with the exception of the YR POD site. Concentrations of these particle-associated PAHs (ng mg<sup>-1</sup> POC) were consistently higher at the York River site (Claybank) but were markedly higher (2x) during October, 1996 and April, 1997. This site has been documented to be a physically dynamic site characterized by high levels of turbidity (up to 400 mg l<sup>-1</sup> at 10 cm above the bed) and extensive physical mixing of the seabed (up to 1 m; Dellapenna et al., 1998). We hypothesize that these enrichments are largely due to variations in sediment transport processes.

Also, with the exception of the April 1997 sample collected from the Mainstem of the CB (Stn 5.4), particle-associated PAHs (e.g., benzo(a)pyrene (BaP), benzo(a)anthracene (BaA), and benzo(g,h,i)perylene) were enriched (ng mg<sup>-1</sup> POC) on particles collected from 1m above the bottom (mab) relative to particles collected from surface waters. This finding may indicate a source for these particle-associated PAHs from resuspended sediments or an enrichment of these components as more reactive organic carbon species are lost during diagenesis.

Ratios of specific pairs of PAH isomers provide useful insights regarding sources of this class of organic contaminants. This approach is more useful than specific compound abundances since isomer pairs are diluted to a similar extent upon mixing with natural particulate matter. The isomer pairs also partition similarly since their thermodynamic and kinetic mass transfer coefficients are comparable. In a preliminary analysis of our data set, we have concentrated on tracing the sources of PAHs that are carcinogenic (BaA and BaP) or have been shown to have tumor initiating activity (benzo[b]fluoranthene; BbF). Again, with the exception of the YR POD site, we find that suspended and sedimentary particulate matter collected from southern CB has remarkably consistent isomer ratios (relative standard error = 1-5%) indicating that the sources of these PAHs are similar throughout this region. Comparing these ratios with those obtained for the major PAH emission sources, the isomer ratios lie predominantly between the values for automobile-derived and coal/industrial sources (Fig. 1).

The relative importance of automobile-derived PAHs decreases progressively from the surface waters to the bottom waters and sediments. Applying a two component mixing model to data collected for particles collected 1 mab, we calculate that 64(±8)% of these carcinogenic PAHs are derived from automobile emissions with the remaining 36(±8)% derived from coal/industrial sources. Only the YR POD site is observed to have a stronger coal/industrial signal for PAHs associated with suspended particulates than at the various other sampling sites in southern CB. Again, this may be the result of anomalous sediment transport processes. In the surficial sediments, we calculate that these PAHs are predominantly derived from coal/industrial sources (80±8%) with the remainder from automobile-emissions. The predominance of coal/industrial-derived PAH carcinogens in surface sediments implies that either automobile-derived PAHs are degraded during transport through the air and waters of the CB or that PAHs in the seabed are dominated by historically or recently deposited coal derived PAHs.



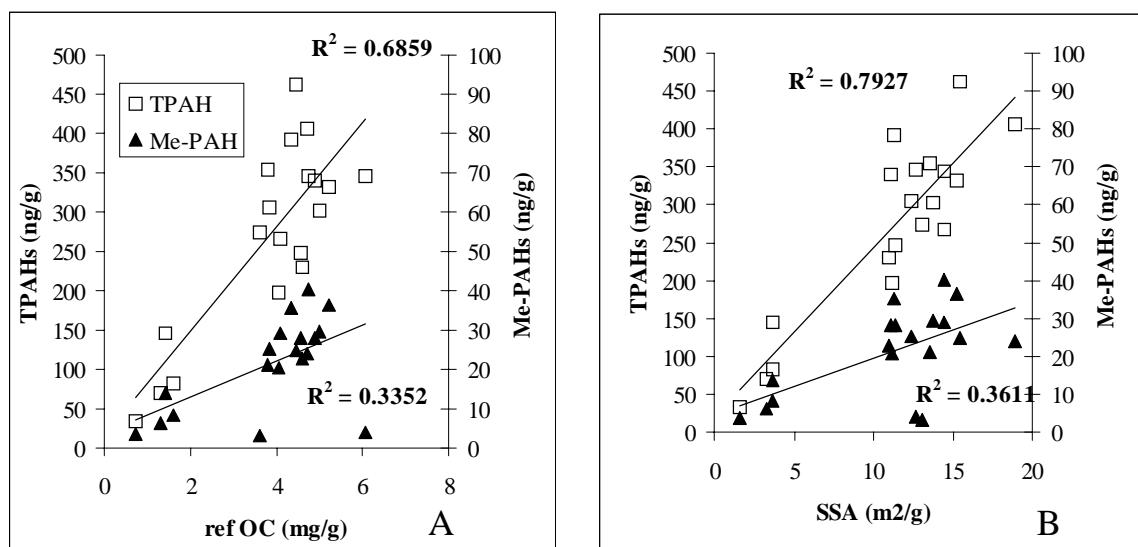
**Fig. 1. Isomer ratios for the four most abundant sources of PAHs and particle samples collected from Chesapeake Bay (A= air particles, R= rain particles, SM= surface microlayer particles, SW= surface water particles, BW=bottom water particles and S = sediments).**  
**Isomer ratios were determined by plotting the isomer concentrations relative to each other and fitting for the slope of the line.**

#### Sources of Particulate Organic Matter

Suspended and sedimentary organic matter in the southern CB appears to be derived from autochthonous sources including a mixture of fresh and detrital phytoplankton, zooplankton and bacteria (Canuel and Zimmerman, in review). The dominant factor contributing to temporal variability during our study appeared to be phytoplankton productivity. Surface particles from the Mainstem sites were enriched in POC (%POC/TSS) during June, 1996. Particles collected from one of the Mainstem sites (WolfTrap) were enriched in lipid during April (%Lipid/TSS) and June (%Lipid/TSS and %Lipid/POC). Concentrations of biomarkers specific to phytoplankton sources (e.g., C<sub>28</sub> sterols) were highest during spring samplings (1996 and 1997). Comparison of sites located at the mouths of two tributaries draining into southern CB (York and Rappahannock Rivers) to two sites located in the Bay mainstem indicated that spatial variation in the sources of POM was not significant in this region of the Bay. The energetic nature of this region of the CB most likely contributes to this homogeneity. Comparison with biomarker studies conducted in other estuaries suggests that the high levels of productivity characteristic of the Chesapeake Bay contribute to high background levels of POM.

## Associations Between PAHs and Sedimentary Organic Matter

We hypothesize that associations with sediment and organic matter phases will influence PAH partitioning between the dissolved and particulate phases, as well as the bioavailability of these contaminants. Increasing our understanding of these associations will be useful in developing models for predicting contaminant behavior in the environment and assessing the risks these sediments pose to organisms, including humans. To this end, a preliminary study was conducted to investigate whether PAHs of different sources (pyrogenic vs. petrogenic) are associated with different sediment and organic matter phases. To examine this, we investigated relationships between pyrogenic and petrogenic PAHs and properties of the sediments (e.g., surface area (SSA) and refractory carbon). In both cases, we find stronger correlations between the non-alkylated PAHs vs. methylated (petrogenic) PAHs and these properties ( $r^2=0.69$  vs. 0.34 for refractory carbon and  $r^2=0.79$  vs. 0.36 for SSA; Fig. 2). Petrogenic PAHs also showed a stronger dependency on sediment concentrations of total extractable lipid, vascular plant derived fatty acids and total nitrogen.



**Fig. 2** Non-alkylated PAHs (TPAH) and methylated PAHs (Me-PAH) are plotted against refractory organic carbon (ref OC) (A) and specific surface area (SSA) (B). Correlation coefficients are statistically significant at  $p<0.05$ .

## **IMPACT/APPLICATION**

Our research has shown the importance of physical and biological processes in determining distributions of natural and contaminant organic matter associated with suspended particles and surficial sediments of a model estuary, southern CB. Results from this study provide insights useful in developing models for predicting contaminant behavior in the environment and assessing the risks these sediments pose to organisms, including humans.

## **TRANSITIONS**

Through coordination of our field efforts, results from this study complement other ONR-funded studies (e.g., Schaffner and others) in the lower Chesapeake Bay.

## RELATED PROJECTS

1. A research grant funded through VA Sea Grant and EPA (to R.M.D.) will support related work in the urbanized Elizabeth River, VA estuary.
2. An NSF supported project (E.A.C.) is currently investigating physical, biological and environmental processes controlling the distribution and lability of organic matter along the entire continuum of the Chesapeake Bay ecosystem. Results from this study will complement those obtained exclusively for the southern region as funded through ONR.

## REFERENCES

Canuel, E.A. and A.R. Zimmerman (in review) Composition of particulate organic matter in the southern Chesapeake Bay: sources and reactivity. *Estuaries*.

Dellapenna, T.M., S.A. Kuehl and L.C. Schaffner (1998) Sea-bed mixing and particle residence times in biologically and physically dominated estuarine systems: a comparison of Lower Chesapeake Bay and the York River subestuary. *Est. Coast. Shelf Sci.*, vol. 46, pp 777-795.

Gustafsson, O., F. Haghseta, C. Chan, J. Macfarlane and P.M. Gschwend (1997) Quantification of the dilute sedimentary soot phase: implications for PAH speciation and bioavailability. *Environ. Sci. Technol.*, vol. 31, pp 203-209.

## PUBLICATIONS

Canuel, E.A. and A.R. Zimmerman. Composition of particulate organic matter in the southern Chesapeake Bay: sources and reactivity. *Estuaries*. In review.

Mitra, S., T.M. Dellapenna, and R.M. Dickhut. 1998. Polycyclic Aromatic Hydrocarbon Deposition and Geochemistry in Lower Hudson River Estuarine Sediments. Currently being revised for publication in *Est. Coast. Shelf Sci.*.

Mitra, S. R.M. Dickhut, S.A. Kuehl, and K.L. Kimbrough. 1998. The Role of Particle Deposition and Geochemistry in Affecting Polycyclic Aromatic Hydrocarbon (PAH) Distribution Coefficients within Estuarine Sediments. Revised manuscript returned to *Mar. Chem.*.

Mitra, S. and R.M. Dickhut. 1998. Three Phase Modeling of PAH Association with Pore Water Dissolved Organic Carbon." Revised manuscript returned to *Environ. Toxicol. Chem.*.